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THE GENERAL CHARACTER OF SPECIFIC HEATS AT HIGH TEMPERATURES

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The wide variations presented by atomic heats at low temperatures have been brought under a single generalization, usually expressed in terms of the quantum hypothesis, in the light of which all follow a common law. This law still demands that at sufficiently high temperatures all atomic heats at constant volume should have the same constant value, approximately 5.96. The applicability of this theory, however, has been doubted; the supposition has been made that the atomic heats continue to increase with temperature, and this has been proved to be true of some metals. The present paper gives data for some non-metallic substances which show the probable existence of such an effect in every case. The substances in question are silica and various silicates. Their specific heats were determined by dropping relatively large charges (50 to 80 grams) from electric furnaces into calorimeters. Temperatures up to 1400° were used in three cases, and up to 1100° at least in most of the others.

The accuracy of the results determines the value of the evidence, and therefore needs attention.[1] (1) As to the 'accidental,' 'visible,' or continually varying errors, the discrepancy between duplicate measurements averaged under 0.5 per mille. Moreover, this small amount of discrepancy was largely accounted for by the irregularity of heat loss in dropping the hissing hot body into water, while this loss, except for its irregularities, was completely canceled out by the procedure used. (2) The unvarying, or systematic, errors were checked by using two each of practically every piece of apparatus, such as furnaces and calorimeters. Comparisons nearly always showed discrepancies under 1 per mille.

The temperature scale was established by means of one of the original Day and Sosman thermoelements, confirmed by numerous concordant metal melting points.

(3) The slowly or occasionally varying errors, the most insidious and detrimental, were checked by repeating some determinations at intervals of several months, with uniformly satisfactory results, and also by general comparisons as in table 1. Here about half the results are compared by giving their differences from a standard fictitious silicate which is approximately the mean of the whole. Of forty-five results above 0° to 100° only three, sporadic ones, those italicized, show discrepancies from a smooth curve exceeding, and then only slightly, the allowed accidental discrepancy of 1 per mille, and, what is perhaps more important, the different comparable series of values, pseudo-wollas-

tonite-diopside-enstatite, and anorthite-andesine-albite, show almost perfect concordance. The temperature distribution in the furnace, the most dangerous source of error, was studied with especial care, and the maximum irregularity detected corresponded to 0.3 per mille. The precautions against systematic error thus appear to be unusually numerous, and the conclusion seems warranted that most of the original results, for mean atomic heats over intervals, are correct to better than 3 per mille, of which less than 1 per mille is accidental.

The method of obtaining from these interval atomic heats the true atomic heats at single temperatures was demonstrably such that original *accidental* errors of 1 per mille might possibly produce single errors of 1% and would be certain to produce single errors of about 5 per mille in a few cases, but would not make any *series* of results wrong by much more than the original error.

TABLE 1

INTERVAL ATOMIC HEATS OF SILICATES, COMPARED BY BEING GIVEN AS DIFFERENCES FROM A FICTITIOUS STANDARD SILICATE

	SILICATE, MINUS STANDARD					
	0°–100°	0°–300°	0°–500°	0°–700°	0°–900°	0°–1100°
$MgSiO_3$ Amphibole	0.023	0.036	0.039	0.039	0.038	0.043
$MgSiO_3$ Pyroxene	0.036	0.059	0.084			
Diopside	0.108	0.109	0.108	0.109	0.109	0.107
$\frac{PW + Py}{2}$	0.129	0.115	0.111			
P. Woll.	0.223	0.170	0.137	0.113	0.093	0.082
Woll.				0.149	0.139	0.136
Anorthite	0.012	(008)	*0.013*	0.001	0.006	0.019
Andesine	−0.055		−0.056	−0.057	−0.053	
$\frac{\text{Anor} + \text{Alb}}{2}$	−0.048		−0.048	−0.056	−0.052	
Albite	−0.107	−0.109	−0.108	−0.113	−0.109	−0.107
Microcline	−0.096	−0.114	−0.112	−0.112	−0.116	*−0.126*
Micro. glass	0.006	*0.003*	0.013	0.017	0.021	0.063
Standard alone	4.067	4.558	4.913	5.143	5.316	5.453

Results.—Results for seven materials are given in table 2 as true mean atomic heats. Of the substances included, silica glass is known to have an almost zero expansion coefficient, hence its atomic heat, though obtained at constant pressure, is the atomic heat at constant volume, or A_v. Cristobalite, a crystalline form of silica, shows a still lower atomic heat, and also shows it up to a considerably higher temperature. Quartz, which also is lower, has a negative coefficient of expansion from 600° to 1000° and the very low value of A_p for cristobalite may be partly or wholly a result of negative expansion. If the small thermal effect of the contraction of quartz is computed and taken into account the result brings A_v up to its value for silica glass, within the uncertainty of the various data.

In order to interpret these results it is necessary to make allowance for the fact that according to the Kinetic Theory, as usually modified to fit the behavior of specific heats at low temperatures, A_v for these oxides is appreciably below 5.96 even at 1300°. Any high-temperature variation must appear as a variation from the value calculated from the low-temperature results. Nernst,[2] using the Nernst-Lindemann formula, has derived a special formula for the atomic heat of silica glass based on determinations from $-247°$ to $+283°$, and this formula, slightly modified to agree with the present results at 283°, at which temperature Nernst had used an approximated value of Magnus', has been used to get the values given in line 5 of table 2.

These values, for 1100° and 1300°, are below the values for cristobalite by more than the probable error, which indicates that unless cristobalite changes very considerably its rate and probable direction of volume change near 1000°, A_v for it is increasing with temperature above the accepted theoretical value. A_v for silica glass is already well above the theoretical curve at 900°, and is probably still further above it at higher temperatures. Unfortunately, this glass could not be continuously heated above 900° without danger of crystallizing. Unlike nearly all the other series the original values for cristobalite were obviously not on a smooth curve, and were smoothed before being used to get the true heats. But none of the changes was above 1 per mille, the permitted accidental error. A very different plausible alteration gave identical results, and none which seemed reasonable gave a value at 1300° lower than 5.83 obtained from the unsmoothed data, and even this value is above the computed curve. For this curve the Debye formula, and even the original Einstein formula, give above 700° results practically identical with those in the table, so the conclusions are not dependent on the particular formula used. Since the theory applies to solid bodies only, and silica glass, being amorphous, has some of the properties of a liquid, the results for cristobalite are more sig-

TABLE 2

ATOMIC HEATS. A_p

	300°	500°	700°	900°	1000°	1100°	1300°
Silica glass	4.95	5.35	5.58	5.75			
Quartz			5.46	5.66			
Cristobalite			5.55	5.67	5.72	5.78	5.86
Silica glass, formula, A_v	4.95	5.35	5.55	5.67	5.71	5.75	5.80
Albite	5.10	5.46	5.71	5.91	5.97		
Microline	5.09	5.47	5.72	5.86	5.92		
Anorthite	5.22	5.58	5.82	6.04	6.14	6.31	6.82
Platinum, A_v		6.45		6.79			6.84

nificant. The values for platinum, given for comparison, were obtained along with the silicates.

Albite and microcline have a smaller proportion of oxygen atoms than silica, and this should bring the theoretical value A_v nearer 5.96 for them than for silica. Moreover, the values of A_p given contain the thermal effect of expansion. Allowances made for these two facts bring these substances into a class with the forms of silica, and thus tend to give assurance that the silica results are not exceptional, although the data are too uncertain to add anything to the exactness of our knowledge of the variations from the theoretical curve.

Anorthite is given as a type of substances showing above 1000° a much larger increase. This increase, however, is very likely in part the effect of the latent heat from a slight amount of melting, due to a very small amount of impurity. Such effects have regularly been found in other kinds of work on silicates. But while such melting can affect the atomic heat as determined for anorthite and most other substances, which crystallize readily on cooling, it can scarcely do the same for the other silicon compounds given here, all of which are very sluggish in their changes of state, so that any slight portion of them melted at the higher temperatures would in all probability merely cool to a glass during the heat determination in the calorimeter, giving out no latent heat. Indeed, since the effect of impurities in causing melting increases rapidly with the temperature, these substances are very exceptional in their value for demonstrations at high temperatures such as that which is the subject of this paper.

Summary.—The specific heats of three forms of silica and two silicates (alkaline feldspars) determined for temperatures up to 1300°, indicate that the atomic heats at constant volume for these substances increase above theoretical value, asymptotic to 5.96, as the heats of metals have been known to do, and hence that such increase is a very general phenomenon, as has been suspected.

[1] A fuller account will be published elsewhere.

[2] Nernst, W., *Ann. Physik, Leipzig*, **36**, 1911, (430).

ON CERTAIN PROJECTIVE GENERALIZATIONS OF METRIC THEOREMS, AND THE CURVES OF DARBOUX AND SEGRE

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About a year ago appeared in these Proceedings an abstract[1] of some investigations which I was then engaged in preparing for publication. As the work progressed it expanded, and I wish to devote this note to a description